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EFFECTS OF AGRONOMIC AND GEOLOGIC FACTORS ON PESTICIDE MOVEMENT IN SOIL: COMPARISON OF TWO GROUND WATER BASINS IN CALIFORNIA

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Abstract

This paper describes the preliminary results of a study conducted by the California Department of Food and Agriculture which compares the soil distribution of herbicides in two ground water basins in the state. In a previous study, residues of several agricultural chemicals were detected in numerous wells in two inland ground water basins, while only one contaminated well was found in two coastal basins. The present study was designed to provide further information on the effects of cultural practices, climatic conditions, and soil and geologic factors in each basin on pesticide mobility.

Soil cores were collected in two citrus-growing regions, one in the San Joaquin Valley, and one on the south coast. Information on agricultural practices and climatic conditions for four years (1981-1984) was obtained from growers and other sources. In order to maximize detection of pesticides in deeper soil layers, sites for soil coring were chosen at locations where the same procedures for application of herbicides had been practiced annually over the same four-year period. Cores were collected in the spring after herbicide application and again in the fall after most of the irrigation water had been applied. Soil samples were analyzed for moisture content, organic carbon content, particle size distribution, and concentrations of three commonly used citrus herbicides, simazine, bromacil and diuron. Where possible, ground water samples were also collected and analyzed. Downward movement of simzaine was monitored in both basins. Within basins we examined the effects of irrigation method on herbicides movement.

In the spring, at the inland sites, simazine was found in soil and ground water samples at 28 feet. At the coastal sites, no simazine was detected deeper than 8 feet below the soil surface, and diuron and bromacil residues occurred only near the surface. Differences between the two basins may be explained in part by the lower organic matter content and higher percentage of sand in the central valley soil. Irrigation method and amount of water applied appeared to have less influence on pesticide movement than soil factors or pesticide chemistry.

Introduction

The objective of the ground water program of the California Department of Food and Agriculture (CDFA) is to formulate a comprehensive plan to minimize the movement of pesticides to ground water as a result of normal application of agricultural chemicals in accordance with California law. In the central San Joaquin Valley numerous wells have tested positive for pesticide residues, whereas in the Santa Clara River Valley, near the southern California coast, only one well contained pesticide residues (Cardozo et al., 1985). The reasons for the occurrence of widespread ground water contamination in one region and only isolated instances in another region have not been adequately explained to date.

The purpose of this study was to examine the soil migration of herbicides in two ground water basins in California in which citrus crops are grown, and to identify soil, geologic, climatic and agronomic factors that could account for differences in pesticide movement between the two basins. We chose sites for soil and ground water sampling in the Kaweah Basin of the San Joaquin Basin Hydrologic Study Area, near the town of Exeter in Tulare County, and in the Ventura Central Basin of the South Coastal Hydrologic Study Area, near the town of Santa Paula in the Santa Clara River Valley, Ventura County (Figure 1). Both basins are considered by the California Department of Water Resources (DWR) to be "subject to critical conditions of overdraft" (DWR, 1980).

The use of simazine in citrus production was originally chosen as the subject of the investigation for two reasons: 1) simazine was previously detected in soil cores (Zalkin et al., 1984); and 2) herbicides are applied annually to perennial crops such as citrus, maximizing the probability of detecting residues in deep soil cores. Later, diuron and bromacil were added to the experimental design in the coastal ground water basin to compare their distribution in the soil profile to that of simazine.

Experimental Design

The design for this study was based on the agricultural practices of cooperating citrus growers. From interviews with growers we discovered that simazine was used in furrow-irrigated citrus groves in both ground water basins. This first contrast, therefore, was a comparison of the distribution of simazine in soil cores under furrow irrigation in the inland basin to cores taken under similar conditions in the coastal basin.

In the coastal region Krovar^{R} (50% bromacil and 50% diuron) was also applied under furrow irrigation, so a second contrast was made: comparison of the vertical distributions of three herbicides, simazine, bromacil and diuron, in soil cores taken from the same ground water basin. A third contrast was made within each basin to compare methods of irrigation. In the inland basin the distribution of simazine under fogger irrigation was compared to that at a site that was historically furrow-irrigated. In the coastal basin, the distributions of bromacil and diuron were compared under drip-in-furrow and furrow irrigation.

A total of five sites were sampled: three in the coastal basin and two

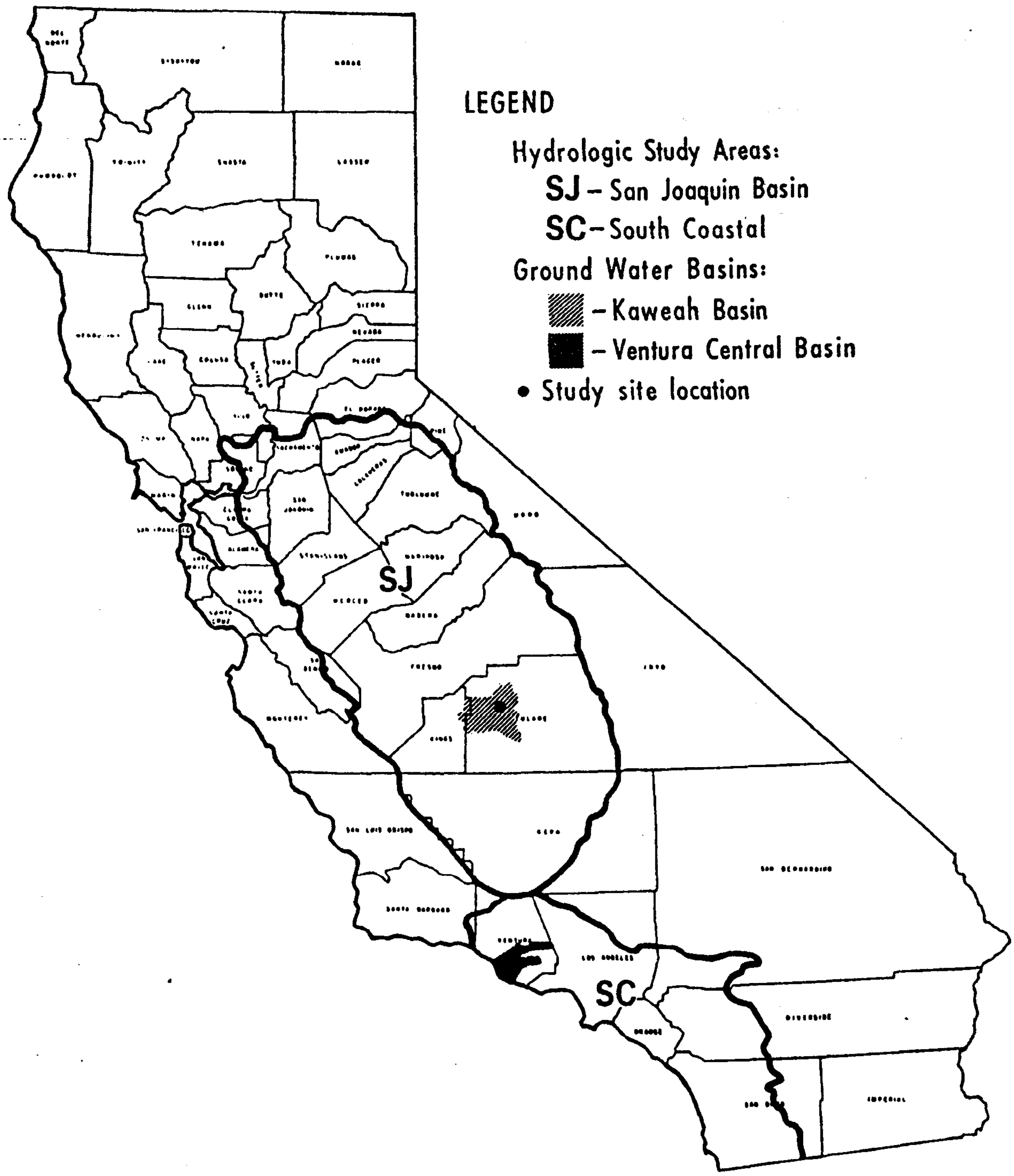

Figure 1. Map of California showing study site locations.

in the inland basin. At each site one core was drilled to approximately 40 feet or to ground water, whichever was shallower, and two other cores were drilled to 15 feet. Each core was divided into six-inch-long segments. Samples from the deepest core were analyzed for herbicide concentration, particle size distribution, organic carbon content, and moisture percent. Samples from the two 15-foot cores were analyzed for herbicides, organic carbon, and moisture.

Drilling took place twice, once in the spring after the spring application of herbicides, and again in the fall after the bulk of irrigation water had been applied but before fall herbicide application. Well water samples were collected in both ground water basins. This report discusses the results of the spring soil sampling and the results of further well sampling in the inland basin.

Site Selection

Both the Santa Clara River Valley and the north central part of Tulare County in the San Joaquin Valley have large acreages planted to citrus. All of the selected sampling sites were located in citrus groves, in alluvial soils with loam surface textures.

Ventura County

Three soil coring sites were chosen at a ranch near Santa Paula, California in the Santa Clara River Valley. According to the Soil Conservation Service (SCS) Soil Survey Report for the Ventura area (1970), all three sites were in Sorrento loam soils, 0-2% slope, of the fine-loamy, mixed,thermic family of Calcic Haploxerolls. These are recent alluvial fan soils with little profile development and high organic carbon content in the top meter (Table 1).

Two sites were located in lemon groves which recieved fall applications of Krovar for control of annual weeds. Site 1 was irrigated by drip lines in furrows and site 2 was furrow-irrigated. The third site was located in a grove of mature Valencia oranges, furrow-irrigated, with fall application of simazine (Table 2).

Tulare County

Two sites were selected in central Tulare County northeast of the town of Exeter. One site was approximately 3/4 mile south of the other. The soil was a San Joaquin loam, of the fine, mixed, thermic family of Abruptic Durixeralfs., with a silica-cemented hardpan overlain by several inches of clay (SCS, 1982). The hardpan contains numerous cracks through which water and plant roots can penetrate, and the claypan varies in thickness. The erosional surfaces on which San Joaquin soils have formed are typically tens of thousands of years old.

Both sites were located in 10-acre Valencia orange groves with simazine and diuron applied in split applications in mid-autumn and early spring (Table 2). Sites 4 and 5 were irrigated by foggers, although site 5 had been furrow-irrigated in previous years. The foggers at site 4 were

Table 1. Comparison of soil and climatic characteristics of coastal (Ventura County) vs inland (Tulare County) site locations.

Characteristic	Coastal Site	Inland Site
Soil Series	Sorrento Loam	San Joaquin Loam
Soil Classification	Calcic Haploxerolls	Abruptic Durixeralfs
Profile Development	Little Development	Highly Developed
Parent Material	Sedimentary Alluvium	Granitic Alluvium
Topographic Position	Alluvial Fan	Low Terrace
Elevation	300 Feet	450 Feet
Slope	0-2%	0-2%
Mean Annual Precipitation	18 Inches	10 Inches
Frost-free Season	300 Days	290 Days
January Maximum Temperature	63° F	57° F
January Minimum Temperature	38° F	37° F
July Maximum Temperature	82° F	100° F
July Minimum Temperature	54° F	66° F

supplemented by furrow irrigation.

Sample Collection and Analysis

Three cores were drilled at each site using a truck-mounted hydraulically driven auger, Mobile Drill Model B-53, with a 20-inch long split barrel sampler containing three six-inch long stainless steel liners. The soil core segments were removed from the sampler in the stainless steel liners. An additional two inches of soil lodged in the cutter shoe of the sampler were discarded when the liners were removed from the split barrel. Each soil-filled liner was covered at both ends with aluminum foil and a plastic cap and then stored on dry ice. This method was designed to produce undisturbed soil samples (Zalkin et al., 1984; Duncan and Oshima, 1985).

In addition to soil samples, ground water samples were obtained whenever possible. When the sample tube reached saturated soil, the tube was removed from the auger and a Teflon^R bailer was attached to the sampling apparatus and lowered into the hole. Water samples were stored in 1-liter amber glass bottles on ice for transport to the laboratory. The bailer was rinsed with 70% isopropanol between uses.

Soil samples were taken to the University of California, Riverside, where they were split into three sections using a hydraulic press. The portion intended for pesticide analysis was collected in a pint glass jar, covered with foil, capped, and stored in a freezer at -20°C until analysis. A second portion was used for determination of gravimetric water content. The pH of the third portion of moist soil was measured using a flat-surface electrode. The soil was then air dried and hydrometer particle-size analysis was performed using 25 g of dry soil (Day, 1965; Flory et al., 1984).

Table 2. Application of pesticide and water to the 5 study sites during the 1984-85 growing season.

Location and Site No.	Herbicides Applied	Application Date	Amount Applied	Irrigation Method	Water Applied[a] Rain	Irrigation	Total
			(lbs/acre)			(acre-feet)	
Ventura County							
Site 1	Bromacil	9/84	2	Drip-in-	0.97	0.19	1.16
	Diuron	9/84	2	Furrow			
Site 2	Bromacil	11/84	2	Furrow	0.68	0.50	1.18
	Diuron	11/84	2				
Site 3	Simazine	11/84	2.8	Furrow	0.68	0.67	1.35
Tulare County							
Site 4	Diuron	11/84	2	Fogger	0.70	0.26	0.96
		3/85	2				
	Simazine	11/84	2				
		3/85	2				
Site 5	Diuron	10/22/84	1.7	Historically	0.70	0.14	0.84
		3/1/85	1.1	furrow with			
	Simazine	10/22/84	2.1	fogger added			
		3/1/85	1.4	in 1984			

[a] For the period between the fall application of herbicide in each site to the date of our spring soil sampling.

Organic carbon content was determined by the Walkley-Black dichromate oxidation method (Nelson and Sommers, 1982).

All pesticide analyses to date have been performed by the Chemistry Laboratory Services Unit of the Department of Food and Agriculture at the Unit's main laboratory in Sacramento. Soil samples were extracted with ethyl acetate and evaporated to near dryness. For simazine residue analysis the extract was dissolved in methanol and analyzed by gas chromatography using a nitrogen specific detector. Extracts for analysis of diuron and bromacil residues were dissolved in acetonitrile and analyzed by HPLC with variable wavelength UV detection. Water samples were analyzed by HPLC and GC with a thermionic specific detector. Pesticide levels are reported in parts per billion (ppb) in both soil and water on a w/w basis.

Well Water Samples

Prior to sampling, well logs were obtained from the state Department of Water Resources. In Tulare County, ten wells which had surface sanitary seals and were less than 150 feet deep were sampled within a 2.5 mile square centered around the core sites. We also sampled two unsealed irrigation wells belonging to one of our original cooperators. These wells were located near the groves in which we took soil samples.

Before any water was collected from a well, the pump was allowed to run for a period sufficient to flush out the casing volume three times. Water samples were taken from a faucet or Schrader valve close to the well and before the storage tank, if pos ible. Samples were collected in one-liter amber glass bottles, and Teflon or stainless steel tubing was used to connect the valve or faucet to the sample bottle when necessary. Filled bottles were covered with foil, capped, and stored on ice.

Results and Discussion

Characterization of Sampling Sites

The Santa Clara River Valley has warm weather year round, with occasional frost in the winter but with an average January high temperature of 63°F. Summer highs are commonly between 80° and 90°F, with night and morning fog from May through August. Most rainfall occurs during the months of November through March. Rainfall can vary from as low as 8 inches to as high as 37 inches in one year, with an average of 18 inches. The annual frost-free season is 300 days (Table 1).

The surface six inches of soil at the coastal basin sites contained approximately 35% sand, 41% silt, and 24% clay, with an average organic carbon content of 2.3%. Organic carbon generally decreased with depth, but remained near one percent throughout the sampling depth. All three sites had one or more lenses of sandy material in the subsurface, and the clay content was below 45% in all samples. Soil pH was close to neutral throughout (Figures 2,3, and 4).

The citrus growing regions of the San Joaquin Valley of California have cool wet winters with dense fog common in December and January. Most of the yearly rainfall occurs between October and April with mean annual precipitation of 10 inches. Freezing temperatures occur infrequently during the winter months. Summers are hot and dry, and high temperatures over 100°F are common. The frost-free season averages 290 days (Table 1).

Particle size analysis revealed average sand, silt, and clay contents of 46.2%, 32.0%, and 21.8%, respectively, in the top six-inch segment of soil. Although both sites were mapped as San Joaquin loam, 0 to 2 percent slope, site 5 had a marked increase in clay, moisture, and organic carbon content at 20 inches, while site 4 decreased in clay and organic carbon at the same depth. Site 4, which received an application of manure and sewage sludge, had an organic carbon content greater than 5% in the top six inches, dropping off rapidly to an average of less than 0.3% below 12 inches. At site 5, where no organic matter was added to the soil surface, the organic

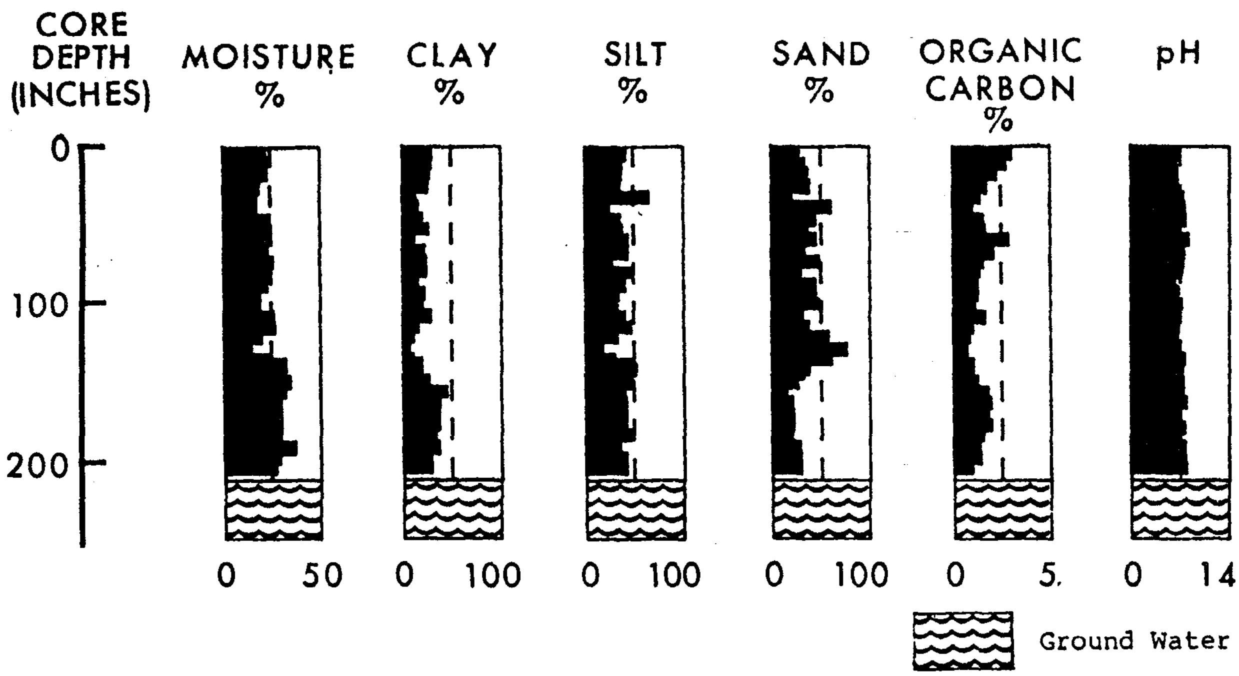

Figure 2. Soil properties to a depth of 17 feet at site 1, Ventura County.

carbon content was very low throughout the profile, with the exception of a bulge from 20 to 50 inches where organic carbon ranged from 0.4 to 0.9% (Figures 5 and 6).

At site 5, moisture and clay profiles reflected the same pattern as organic carbon. Particle size analysis of samples from site 4 indicated no accumulation of clay at the 20 to 50 inch depth. It has long been common practice to rip the soil before planting trees in this region, and the process of ripping mixes the soil horizons. This could account for the low clay percentage above the hardpan in site 4, or it could simple be the result of local variability. At both sites soil pH stayed near neutral throughout the profile.

Comparison between basins

In the coastal basin (site 3) simazine was recovered from the top 86 inches of the soil profile. The highest concentration was in the 0-6 inch segment, averaging 230 ppb (Table 3), followed by a rapid decrease in concentration with depth to near 2 ppb in the 80-86 inch segment. Site 5, the comparable inland location, averaged on 87 ppb in the soil surface, with the concentration dropping below 10 ppb from 6 to 12 inches (Table 3). Few of the samples from site 5 (7 of 24, or 29%) contained any simazine, at an MDL of 5 ppb, in the upper 52 inches of the profile, while simazine was detected in 18 of 22 (82%) of the 0-52 inch samples from site 3. During the soil coring process in April 1985, ground water samples were collected from the Tulare County sites at 28 feet. The average simazine concentration in ground water at site 5 was 0.9 ppb.

Mass balance calculations, based on a bulk density of 1.5% c/cm^3, were made for both sites to compare the amount of simazine that was recovered to

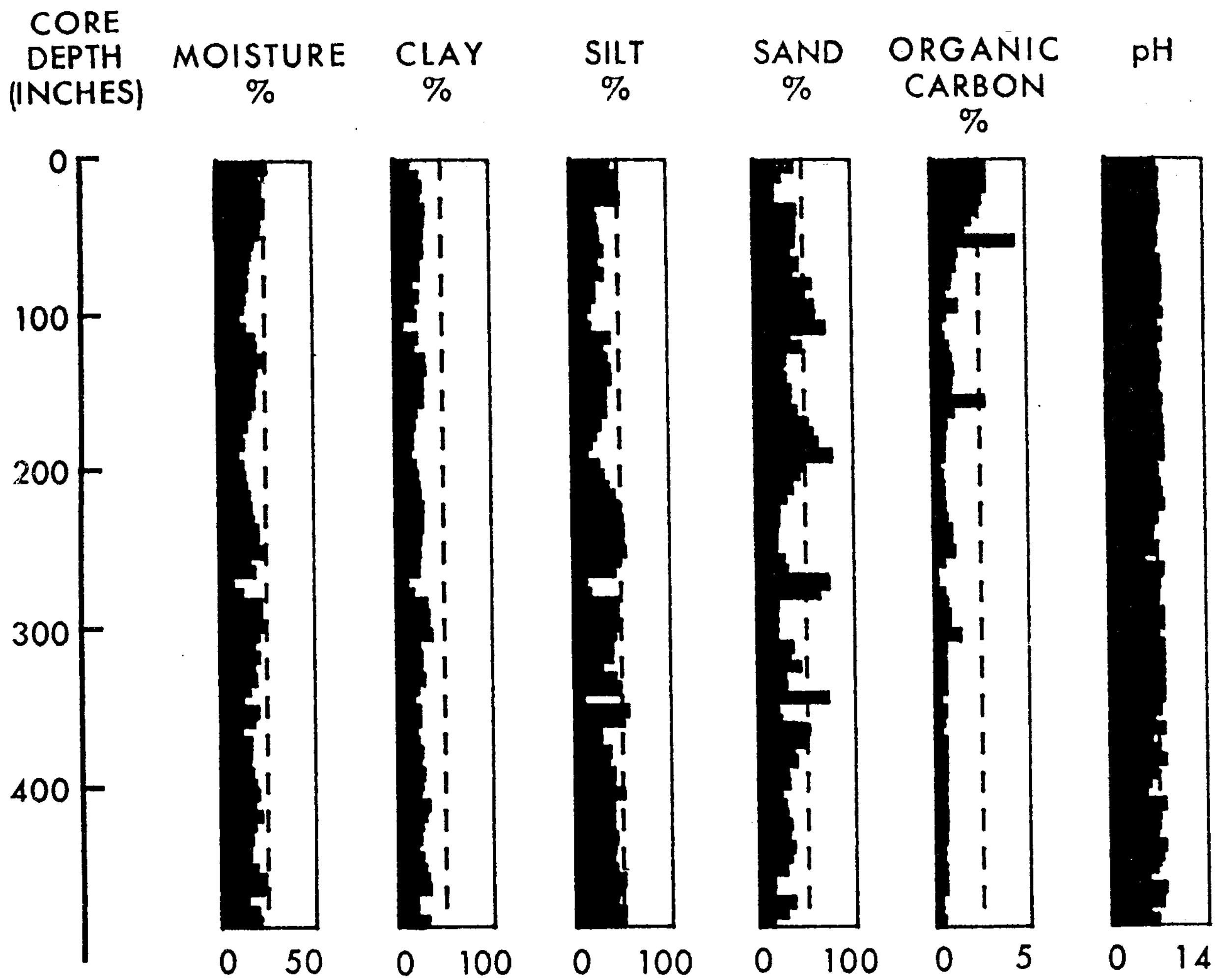

Figure 3. Soil properties to a depth of 40 feet at site 2, Ventura County.

the amount originally applied. In Ventura County, simazine was applied at a rate of 2.8 lb active ingredient (ai) per acre (3.14 kg/ha) in November 1984 while 0.7 ai/ac (0.8kg/ha) was recovered from the soil samples collected in April 1985, five months later. The amount of simazine recovered was 25% of the amount applied. In Tulare County, 2.1 and 1.4 lb ai/ac (2.35 and 1.57 kg/ha) were applied in November 1984 and March 1985, respectively, and 0.22 lb ai/ac (0.25 kg/ha) was recovered from the soil cores taken in April 1985, approximately one month after the spring application. Based on the total amount of simazine applied during the season, 6.4% of the simazine was recovered, but based only on the spring application the recovery rate was 16.1%.

Much less simazine was recovered in soil from the inland basin than in the coastal basin. This difference cannot be the result of differences in amount of water applied, because the inland sites received less water (irrigation plus rainfall) than the coastal sites during the period between fall herbicide application and soil sampling (Table 2). Assuming first order kinetics, the soil half-life of simazine in the coastal basin was 70 days, based on our calculated recovery rate. This agrees reasonable well with published values (Table 4). The half-life and the organic carbon content of

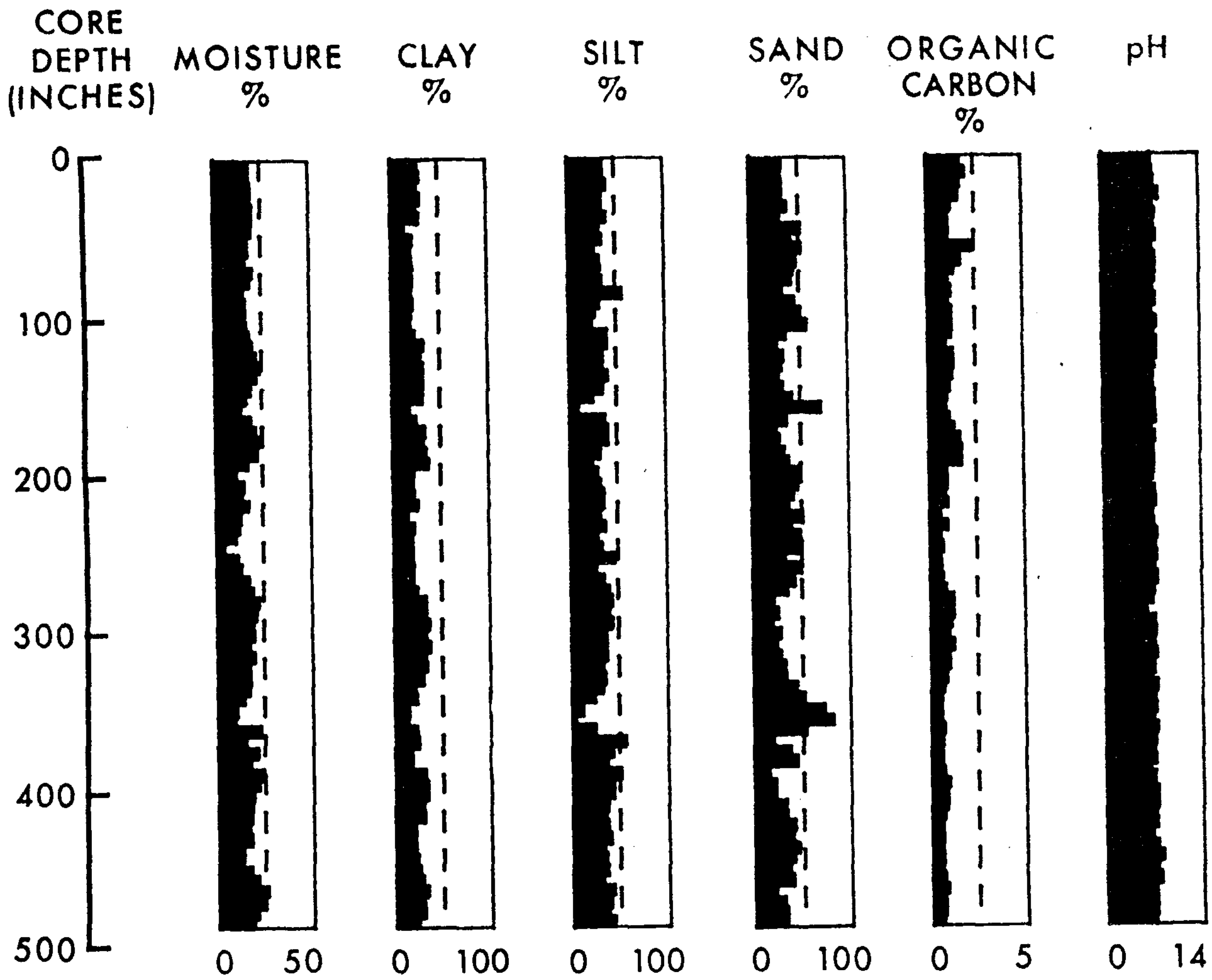

Figure 4. Soil properties to a depth of 40 feet at site 3, Ventura County.

the coastal soil indicate that microbial and chemical degradation could account for the disappearance of simazine from the profile.

In contrast, the calculated half-life for simazine in the inland basin was 16 days, a value too low for dissipation to be attributed solely to microbial degradation. The presence of simazine in ground water, along with the low organic carbon content and sandy subsoil, suggest that in the inland basin leaching was another avenue for loss of the chemical from the system.

Comparison of herbicides

Simazine, bromacil, and diuron, all of which were applied to sites in the coastal ground water basin, were distributed in distinctly different patterns in the soil profile (Table 3 and 5, comparison of furrow-irrigated sites). Although it must be noted that each pesticide had a different minimum detectable level (MDL), so that comparisons were limited by the pesticide with the highest MDL, the difference between simazine and diuron was most

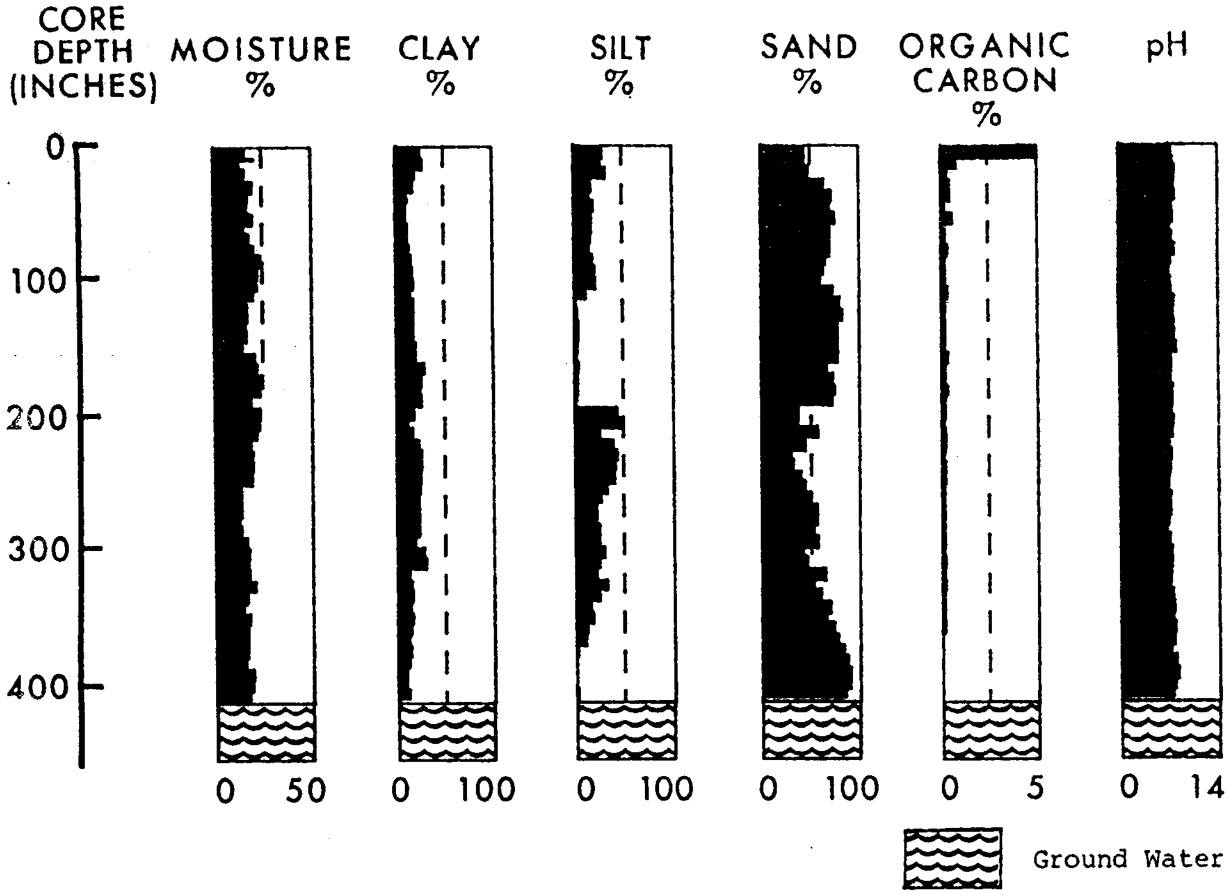

Figure 5. Soil properties to a depth of 28 feet at site 4, Tulare County.

obvious. The average concentration of diuron in the top 6 inches at site 2 was 660 ppb (Table 5). Diuron was not detected below 12 inches at an MDL of 10 ppb. The amount of diuron recovered from the soil was equal to 1.38 lbs ai/acre, or 68% of the 2.0 lbs ai/acre applied in November 1984. In contrast, at site 3, 14 out of 22 segments above 52 inches contained more than 10 ppb simazine (Table 3).

Bromacil, with an MDL of 20 ppb, appeared deeper in the soil profile than diuron, but not as deep as simazine. The average concentration of bromacil was 223 ppb in the top 12 inches and 92 ppb from 12 to 18 inches. No bromacil was detected below 32 inches, but because of missing data and the high MDL these results must be interpreted cautiously. Results of well sampling in Ventura County (MDL = 0.1 ppb) may demonstrate whether bromacil is moving deeper in the profile than soil analyses indicate.

The order of mobility in the coastal basin soil appeared to be simazine > bromacil > diuron. The relatively small differences in amounts of water applied could not have accounted for the differences in movement (Table 2). Although simazine was applied at higher rates than either of the other compounds, its soil half-life and water solubility are significantly lower. Bromacil has the lowest K_d and K_{oc} values, which indicates that bromacil has the least attraction to soil components of the three herbicides (Table 4). One would expect, therefore, to find bromacil at greater depths than diuron

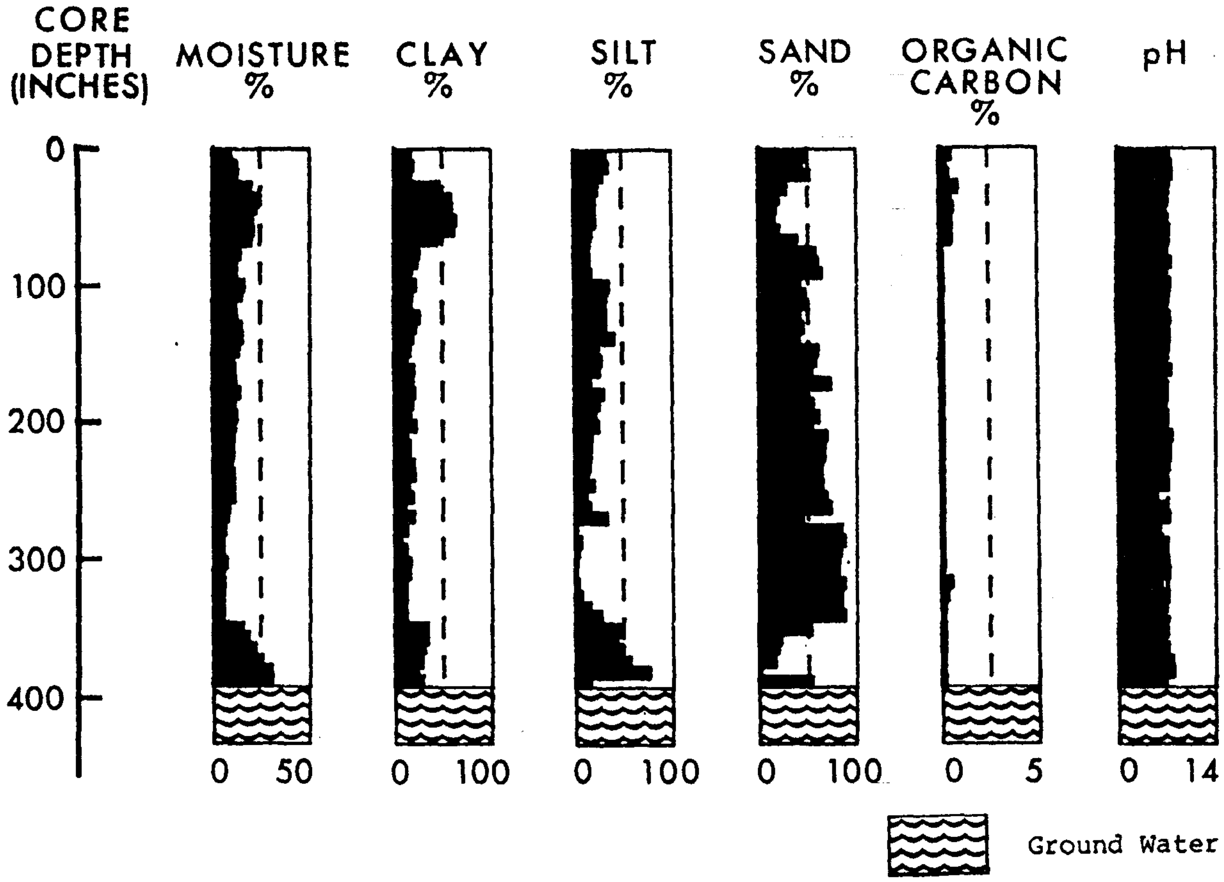

Figure 6. Soil properties to a depth of 28 feet at site 5, Tulare County.

or simazine. It appears that parameters such as K_d need to be calculated differently to reflect field conditions, or that factors other than pesticide chemistry and soil degradation rate are involved in determining relative mobility.

Effect of irrigation method on pesticide movement: Coastal basin

Both the furrow-irrigated field (site 2) and drip-in-furrow irrigated field (site 1) received approximately equal amounts of water during the post-herbicide application period (Table 2). The two sites showed similar distributions of the applied herbicides: most of the diuron occurred in the top 12 inches, while significant amounts of bromacil were recovered from the 12-26 inch section (Table 5). Neither bromacil nor diuron was detected in ground water samples obtained at 17 feet from the drip-in-furrow-irrigated site. However, a greater amount of bromacil and diuron was recovered from the soil samples from site 1 than from site 2 (68.6% of the bromacil and 90.2% of the diuron for site 1, versus 55.7% of bromacil and 68.6% of diuron for site 2). Irrigation method may have an influence on pesticide degradation rate, but this needs further investigation.

Effects of irrigation method: Inland basin

In the field that was historically furrow-irrigated (site 5), very little simazine was recovered (Table 3). No simazine was detected from 32 to 56

Table 3. Distribution of simazine to 15 foot depth in 3 replicate soil cores obtained at the coastal site and at the two inland sites.

SEGMENT DEPTH	COASTAL SITE			INLAND SITES					
	FURROW IRRIGATION[a]			FURROW IRRIGATION[b]			FOGGER IRRIGATION[c]		
(INCHES)	1	2	3	1	2	3	1	2	3
0-6	120[d]	380	190	31	10	220	12	5	10
6-12	15	56	45	6	ND	7	ND	ND	ND
12-18	–[e]	ND[f]	–	ND	ND	ND	5	ND	ND
20-26	18	20	18	7	50	ND	ND	ND	ND
26-32	ND	17	24	ND	ND	ND	ND	ND	ND
32-38	10	35	30	ND	ND	ND	ND	ND	–
40-46	6	6	9	ND	ND	ND	–	–	–
46-52	ND	ND	20	ND	ND	ND	ND	5	ND
52-58	ND	3	8	–	ND	ND	–	2	ND
60-66	–	2	1	–	–	ND	ND	ND	ND
66-72	ND	2	6	ND	–	ND	–	2	ND
72-78	–	ND	5	ND	–	ND	–	ND	–
80-86	ND	ND	–	ND	ND	ND	ND	2	ND
86-92	ND	ND	2	ND	ND	ND	ND	ND	2
92-98	–	ND	ND	ND	ND	–	ND	–	–
100-106	ND	ND	ND	ND	ND	ND	ND	ND	ND
106-112	ND	ND	ND	ND	–	–	ND	ND	ND
112-118	ND	ND	ND	ND	ND	–	1	ND	ND
120-126	ND	ND	ND	–	–	ND	–	–	ND
126-132	ND	ND	ND	–	ND	ND	ND	ND	ND
132-138	ND	ND	ND	ND	ND	ND	ND	ND	–
140-146	ND	ND	–	ND	ND	ND	ND	ND	–
146-152	ND	ND	ND	ND	ND	–	ND	ND	ND
152-158	ND	ND	ND	–	–	ND	–	–	–
160-166	ND	ND	ND	–	–	–	–	ND	2
166-172	ND	ND	ND	–	–	ND	–	ND	–
172-178	ND	ND	ND	ND	ND	ND	–	ND	–

[a] Denoted site 3 in text.
[b] Denoted site 5 in text.
[c] Denoted site 4 in text.
[d] Values in ppb.
[e] No sample
[f] Not detected at 5 ppb (0-52") or 1 ppb MDL

Table 4. Summary of chemical parameters related to soil mobility for simazine, bromacil and diuron.

Pesticide	Chemical Name	Water Solubility	Soil Half-life	K_d	K_{oc}	Molecular Weight
Bromacil	5-bromo-3-sec-butyl-6-methyluracil	815 ppm (77° F)	5-6 months [a] 106 days [b,c] 90 days [b,c] 349 days [b,d]	0.3 [e] 0.2-1.8 [a]	72 [b] 69-77 [a]	261.10
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea	42 ppm (77° F)	328 days [d]	8.9 [b] 5.4 [i]	382.6 [b]	233.10
Simazine	2-chloro-5-6 bis(ethylamino)-s-triazine	3.5 ppm (68° F)	37 days [f,g] 234 days [f,h] 75 days [b,c] 64 days [b,d]	2.3 [b,e,i]	138.4 [e]	201.66

[a] Cohen et al, 1984
[b] Rao and Davidson, 1980
[c] Laboratory study
[d] Field study
[e] Dean et al, 1984
[f] Walker, 1976
[g] Measured at 77° F and 13% moisture content
[h] Measured at 59° F and 7% moisture content
[i] Knisel, 1980

Table 5. Distribution of diuron and bromacil to 15 foot depth in 3 replicate cores obtained at each coastal site.

SEGMENT DEPTH	FURROW IRRIGATION[a]						DRIP-IN-FURROW IRRIGATION[b]					
	DIURON			BROMACIL			DIURON			BROMACIL		
(INCHES)	1	2	3	1	2	3	1	2	3	1	2	3
0-6	800[c]	440	750	210	260	200	510	–[d]	810	600	100	180
6-12	18	12	ND[e]	360	170	140	ND	28	420	70	150	210
12-18	ND	–	–	200	ND	75	ND	ND	28	44	79	320
20-26	–	ND	ND	–	ND	25	ND	ND	ND	ND	50	ND
26-32	ND	ND	–	ND	ND	–	ND	–	ND	ND	–	ND
32-38	–	ND	–	–	ND	–	ND	ND	ND	ND	ND	ND
40-46	–	ND	–	–	ND	–	ND	ND	ND	ND	ND	ND
46-52	ND	ND	–	ND	ND	–	ND	ND	ND	ND	ND	ND
52-58	–	ND	ND	–	ND	ND	ND	ND	–	ND	ND	–
60-66	ND	ND	–	ND	ND	–	–	ND	ND	–	ND	ND
66-72	ND	–	–	ND	–	–	ND	–	ND	ND	–	ND
72-78	ND	ND	ND	ND	ND	ND	ND	ND	–	ND	ND	–
80-86	ND	–	–	ND	–	–	ND	ND	–	ND	ND	–
86-92	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
92-98	ND	ND	ND	ND	ND	ND	ND	ND	–	ND	ND	–
100-106	ND	–	ND	ND	–	ND	ND	ND	–	ND	ND	–
106-112	ND	–	–	ND	ND	–	–	–	–	–	–	–
112-118	–	–	ND	–	–	ND	ND	–	–	ND	–	–
120-126	ND	–	–	ND	–	–	ND	ND	ND	ND	ND	ND
126-132	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
132-138	ND	ND	ND	ND	ND	ND	ND	–	–	ND	–	–
140-146	ND	–	–	ND	–	–	–	ND	–	–	ND	–
146-152	ND	ND	ND	ND	ND	ND	ND	ND	–	ND	ND	–
152-158	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
160-166	–	–	–	–	–	–	ND	ND	–	ND	ND	–
166-172	ND	–	ND	ND	–	ND	ND	ND	–	ND	ND	–
172-178	ND	ND	ND	ND	ND	ND	–	ND	ND	–	ND	ND

[a] Denoted site 2 in text.
[b] Denoted site 1 in text.
[c] Values in ppb.
[d] No sample.
[e] Not detected at an MDL of 10 ppb for diuron and 20 ppb for bromacil.

Table 6. Concentrations of simazine and diuron in well water sampled in January 1986 at the inland basin locations.

Well Number	Herbicide	Initial Sampling[a]	Confirmation Sample
1	Simazine	N.D., N.D.[b]	N.D.
	Diuron	N.D., N.D.	
2	Simazine	N.D., N.D.	N.D.
	Diuron	N.D., N.D.	
3	Simazine	0.65, 0.78[c]	0.75
	Diuron	0.61, 0.66	0.60
4	Simazine	0.65, 0.65	0.56
	Diuron	1.10, 1.20	1.30
5	Simazine	N.D., 0.38	N.D.
	Diuron	0.70, 0.70	0.60
6	Simazine	0.45, 0.90	0.38
	Diuron	0.60, 0.80	0.60
7	Simazine	0.10, 0.20	0.10
	Diuron	N.D., 0.10	N.D.
8	Simazine	N.D., N.D.	N.D.
	Diuron	N.D., 0.20	N.D.
9	Simazine	0.31, 0.34	0.30
	Diuron	0.64, 0.65	0.60
10	Simazine	0.55, 0.55	0.50
	Diuron	0.70, 0.81	0.72
11[d]	Simazine	0.78, 0.78	-[e]
	Diuron	0.40, 0.45	-
12[d]	Simazine	N.D., N.D.	-
	Diuron	N.D., N.D.	-

[a] Replicate samples were analyzed.

[b] None detected at MDL of 0.1 ppb for both compounds.

[c] Values reported in parts per billion.

[d] Unsealed irrigation wells.

[e] Not sampled.

inches at an MDL of 5 ppb, or below 52 inches at an MDL of 1 ppb. Simazine was detected in replicate water samples at approximately 1 ppb. At the site that was historically fogger-irrigated (site 4), 1 to 2 ppb of simazine were detected in segments distributed throughout the soil profile. Replicate ground water samples collected at this site at a depth of 28 feet contained approximately 4 ppb of simazine.

The amount of simazine recovered at site 4 was 0.03 lb ai/ac (0.03 kg/ha). Compared to the application rate of 2.0 lb ai/ac (2.24 kg/ha) in November 1984 and again in March 1985, the amount recovered was 0.8% of the total application for the season and 1.5% of the spring application. Although this is a lower percentage than recovered at site 5 (16% of the spring application), both recovery rates were low in light of the short time (approximately one month) between spring application and soil coring. The lower recovery rate at site 4 may have been related to the application of manure to the soil surface: the extra organic matter in the 0 to 6 inch segment may have resulted in increased adsorption of simazine, allowing for accelerated degradation of the pesticide by microorganisms in this region of the profile (Burges, 1970). However, the low simazine recovery and the detection of simazine in ground water in both locations indicate that either irrigation method was capable of causing redistribution of simazine through the profile.

Herbicide Residue in Well Water

To test our hypothesis that simazine was travelling through the soil profile to ground water in Tulare County, we decided to sample wells in the vicinities of the soil coring sites. Although the first set of soil samples was not analyzed for diuron, the Tulare County citrus groves had received applications of that compound, and we therefore chose to analyze well samples for both simazine and diuron.

In January 1986 twelve wells in Tulare County were sampled. Nine of the wells were found to contain residues of simazine, diuron or both. Ten of the 12 wells were resampled for confirmation in March and seven of the ten tested positive for one or both chemicals. All concentrations were less than 2 parts per billion (Table 6).

Summary

Soil cores were obtained to compare the soil distribution of citrus herbicides in a coastal ground water basin located in Ventura County, California, and an inland basin in Tulare County. Data on history of agricultural practices, on physical and chemical characteristics of surface and subsurface soil, and on chemical characteristics of the herbicides, were collected.

Simazine was detected to a depth of 86 inches in the coastal basin. The highest average concentration was in the first six inches (230 ppb), decreasing with depth until 2.0 ppb were detected in the 80 to 86 inch segment. The amount of simazine recovered from soil samples indicated a soil half-life of approximately 70 days, which agreed with previous estimates

of microbial degradation of simazine in soil. The organic carbon content of the coastal soil was approximately 2.3% in the surface and around 1% in the subsurface to a depth of 35 feet. This was probably the major factor in the observed distribution of simazine. In contrast, simazine was detected in the inland basin at approximately 1 ppb in ground water samples obtained at 28 feet. Much less simazine was recovered from the surface soil (87 ppb in the first six inches) and a more random distribution was measured even within the top 18 inches. The amount of simazine recovered corresponded to a soil half-life of 16 days, which indicated that leaching, not microbial degradation, was a major mechanism in dissipation of the compound. The major factors contributing to pesticide movement in this area were the low organic carbon content of these soils, generally below 0.5% throughout the profile, and the predominantly sandy subsoil.

The soil distribution of herbicides at the coastal sites indicated an order of mobility of simazine > bromacil > diuron. Compared at the minimum detectable level for bromacil (20 ppb), diuron was recovered at a depth of 12 inches, bromacil to 18 inches, and simazine was detected down to 52 inches. One might expect greater mobility for bromacil than simazine because bromacil has a higher water solubility, longer soil half-life and the lowest K_d and K_{oc} values.

Similar distributions of bromacil and diuron were obtained under different methods of irrigation in the coastal soil. Irrigation method also did not appear to influence simazine distribution at the inland sites. Thus, geologic factors may override current agronomic factors in determining site sensitivity to pesticide movement and ground water contamination under specific cropping patterns. The relationship between physical properties of soils and chemical properties of pesticides, as they relate to pesticide mobility, needs further investigation.

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References

Burges, Alan. 1970. The soil microflora--its nature and biology. In Ecology of Soil-Borne Plant Pathogens. K.F. Baker and W.C. Snyder, eds. UC Press. Berkeley. pp. 21-31.

Cardozo, C., S. Nicosia, and J. Troiano. 1985. Agricultural Pesticide Residues in California Well Water: Development and Summary of a Well Inventory Data Base for Non-Point Sources. California Department of Food and Agriculture. Sacramento, CA. 65 pp.

Cohen, S.Z., S.M. Creeger, R.F. Carsel and C.G. Enfield. 1984. Potential for Pesticide Contamination of Ground Water resulting from Agricultural Uses. In Treatment and Disposal of Pesticide Wastes, Americal Chemical Society Symposium Series.

Day, Paul. 1965. Particle fractionation and particle-size analysis. In

Methods of Soil Analysis. Part 1: Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling. C.A. Black, ed. American Society of Agronomy. Madison, WI. pp. 545-567.

Dean, J.D., P.P. Jowise and A.S. Donigian, Jr. 1984. Leaching Evaluation of Agricultural Chemicals: a Handbook. U.S. Environmental Protection Agency. Washington, D.C. 407 pp.

Department of Water Resources. 1980. Ground Water Basins in California. Report to the Legislature in Response to Water Code Section 12924. DWR Bulletin 118-80, 79 pp. Sacramento, CA.

Duncan, D.W. and R.J. Oshima. 1985. Ethylene Dibromide in Two Soil Profiles. California Department of Food and Agriculture. Sacramento, CA. 56 pp.

Elford, C. Robert. 1970. Climatography of the United States. U.S. Department of Commerce. Publication No. 60-4. Washington, D.C.

Flory, R., T.T. Kato and H. Stensrud. 1984. Review of analytical methods utilized by Environmental Hazards Assessment Program. California State University. Chico, CA. 8 pp.

Knisel, W.G., ed. 1980. CREAMS: A Field-Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems. U.S. Department of Agriculture, Conservation Research Report No. 26. Washington, D.C. 643 pp.

Nelson, D.W. and L.E. Sommers. 1982. Total Carbon, Organic Carbon, and Organic Matter. In Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties. 2nd edition. A.L. Page, editor. American Society of Agronomy. Madison, WI. pp. 539-579.

Rao, P.S.C. and J.M. Davidson. 1980. Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollution Models. In Environmental Impact of Nonpoint Source Pollution, M.R. Overcash and J.M. Davidson, eds. Ann Arbor Science. Ann Arbor, MI. pp. 23-69.

Soil Conservation Service. 1982. Soil Survey of Central Tulare County. U.S. Department of Agriculture. Washington, D.C.

Soil Conservation Service. 1970. Soil Survey of the Ventura Area. U.S. Department of Agriculture. Washington, D.C.

Walker, A. 1976. Simulation of Herbicide Persistence in Soil. I. Simazine and Prometryne. Pesticide Science, v.7, pp. 41-49.

Zalkin, F., M. Wilkerson and R.J. Oshima. 1984. Pesticide Movement to Ground Water. Volume II. Pesticide Contamination in the Soil Profile at DBCP, EDB, Simazine and Carbofuran Application Sites. California Department of Food and Agriculture. Sacramento, CA. 168 pp.

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